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**Ozawa et al.**

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(54) **TONER**

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(58) **Field of Classification Search**  
CPC ..... *G03G 9/093*; *G03G 9/09307*  
See application file for complete search history.

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(56) **References Cited**

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(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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Jan. 27, 2014 (JP) ..... 2014-012357

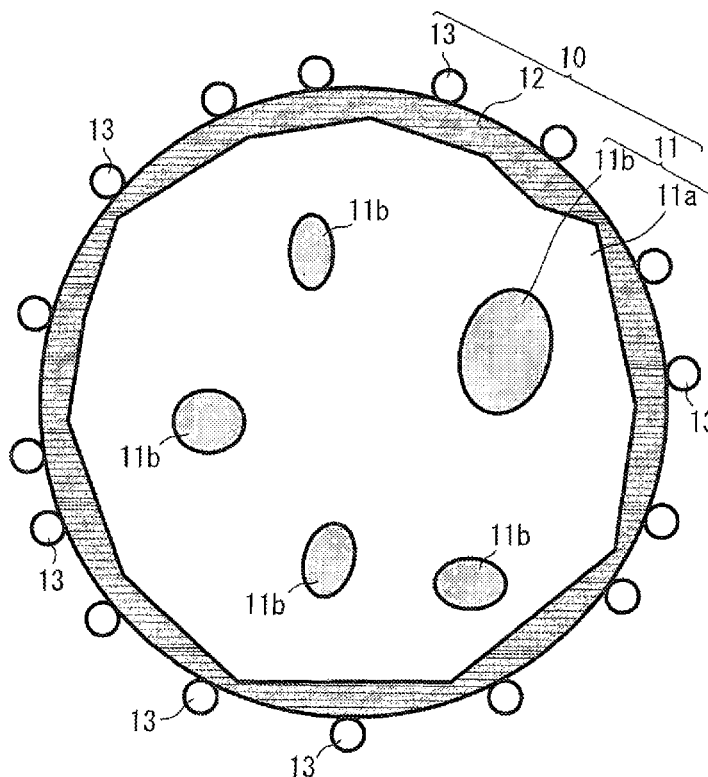
(51) **Int. Cl.**  
*G03G 9/093* (2006.01)

(52) **U.S. Cl.**  
CPC ..... *G03G 9/09314* (2013.01); *G03G 9/09321*

(57) **ABSTRACT**

A toner includes toner particles each including a core and a shell layer disposed over a surface thereof. The shell layers contain a unit derived from a thermoplastic resin and a unit derived from a monomer or prepolymer of a thermosetting resin. Young's moduli of the shell layers and the cores, as measured using an SPM while raising cantilever temperature thereof, satisfy conditions:  $X2/X1$  is at least 2.0 and no greater than 5.0; and  $Y2/Y1$  is at least 4.0 and no greater than 7.0.  $X1$  denotes a proportion of change of the Young's modulus of the shell layers and  $X2$  denotes a proportion of change of the Young's modulus of the cores from 30° C. to 50° C.  $Y1$  denotes a proportion of change of the Young's modulus of the shell layers and  $Y2$  denotes a proportion of change of the Young's modulus of the cores from 50° C. to 70° C.

**5 Claims, 3 Drawing Sheets**



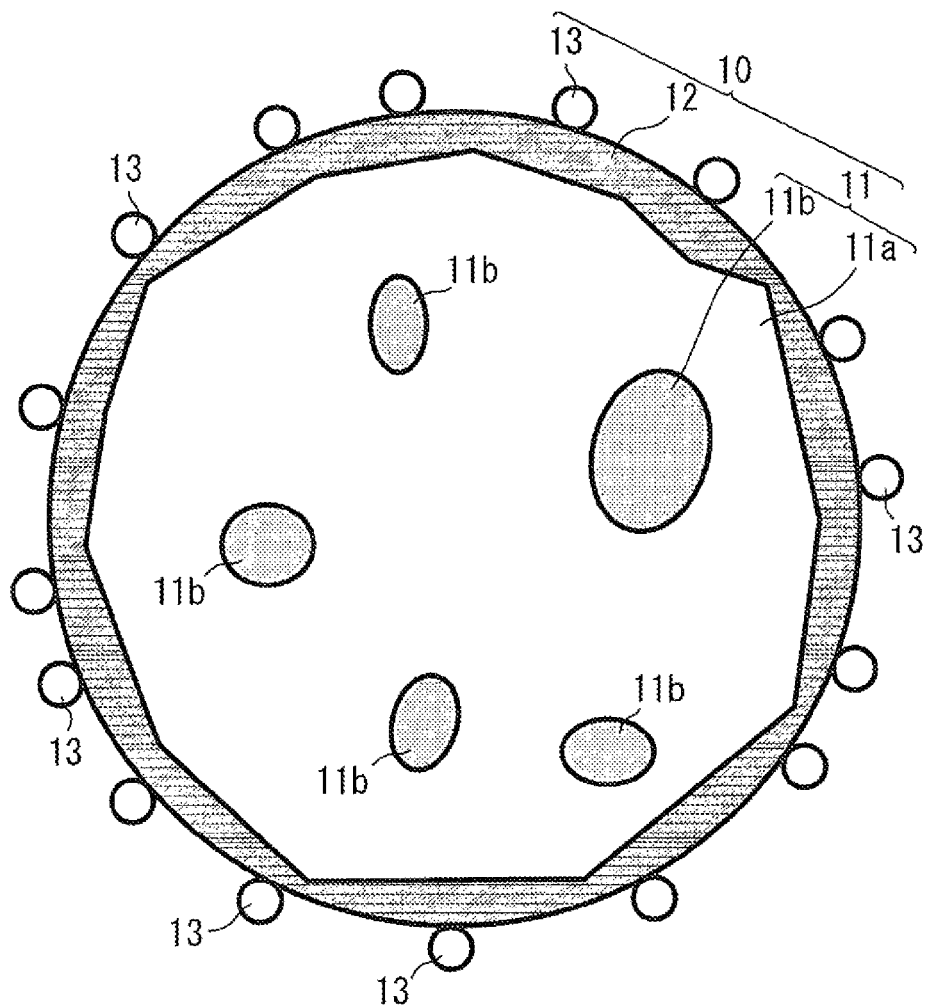


FIG. 1

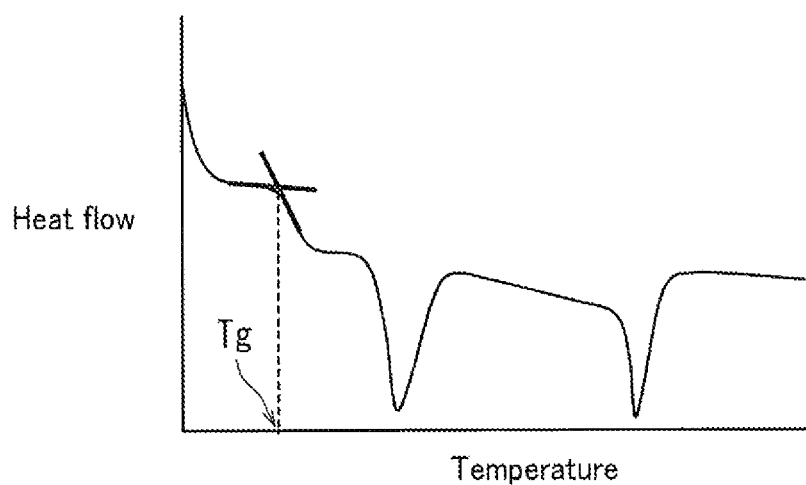


FIG. 2

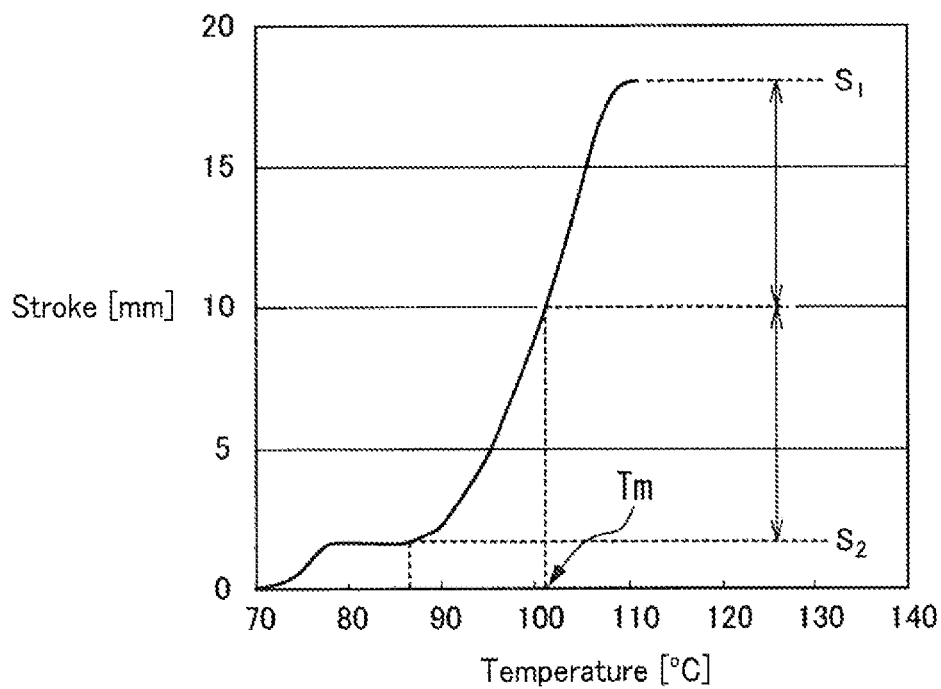


FIG. 3

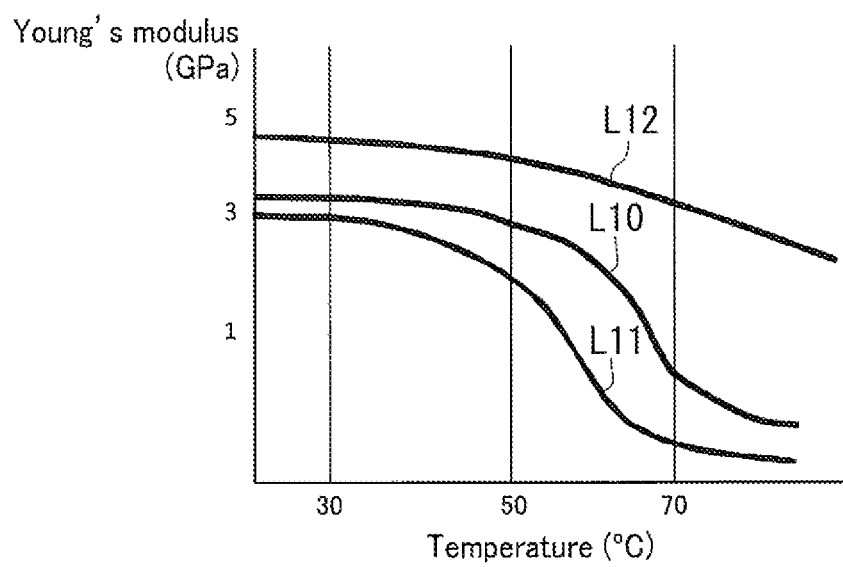


FIG. 4

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## TONER

### INCORPORATION BY REFERENCE

The present application claims priority under 35 U.S.C. §119 to Japanese Patent Application No. 2014-012357, filed Jan. 27, 2014. The contents of this application are incorporated herein by reference in their entirety.

### BACKGROUND

The present disclosure relates to a toner and in particular relates to a capsule toner.

A capsule toner includes toner particles that each include a core and a shell layer (capsule layer) disposed over the surface of the core. For example, in a known method of manufacturing a capsule toner, shell layers are formed using resin particles (specifically, acrylic resin particles) having a Martens hardness of at least 120 N/mm<sup>2</sup> and no greater than 180 N/mm<sup>2</sup>.

### SUMMARY

A toner according to the present disclosure includes a plurality of toner particles each including a core and a shell layer disposed over a surface of the core. The shell layer contains a unit derived from a thermoplastic resin and a unit derived from a monomer or prepolymer of a thermosetting resin. A Young's modulus of the core and a Young's modulus of the shell layer, as measured using a scanning probe microscope while raising a cantilever temperature thereof, satisfy conditions: X2/X1 is at least 2.0 and no greater than 5.0; and Y2/Y1 is at least 4.0 and no greater than 7.0. X1 denotes a proportion of change of the Young's modulus of the shell layer upon raising the cantilever temperature from 30° C. to 50° C. X2 denotes a proportion of change of the Young's modulus of the core upon raising the cantilever temperature from 30° C. to 50° C. Y1 denotes a proportion of change of the Young's modulus of the shell layer upon raising the cantilever temperature from 50° C. to 70° C. Y2 denotes a proportion of change of the Young's modulus of the core upon raising the cantilever temperature from 50° C. to 70° C.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a toner particle included in a toner according to an embodiment of the present disclosure.

FIG. 2 illustrates a method of reading a glass transition point from a heat absorption curve.

FIG. 3 illustrates a method of reading a softening point from an S-shaped curve.

FIG. 4 is a graph illustrating a relationship between Young's modulus and temperature for a thermoplastic resin, a thermosetting resin, and a composite resin.

### DETAILED DESCRIPTION

The following explains an embodiment of the present disclosure.

A toner according to the present embodiment is a capsule toner for developing an electrostatic charge image. The toner according to the present embodiment is for example suitable for use as a positively chargeable toner for developing an electrostatic charge image. The toner according to the present embodiment is a powder including a large number of particles (herein referred to as toner particles). The toner may be used as a one-component developer. Alternatively, the toner may

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be mixed with a carrier using a mixer (for example, a ball mill) in order to prepare a two-component developer. The toner according to the present embodiment can for example be used in an electrophotographic apparatus (image forming apparatus).

The following explains an example of an image forming method performed by the electrophotographic apparatus. First, an electrostatic charge image is formed on a photosensitive body based on image data. Next, the formed electrostatic charge is developed using a developer containing the toner. In the development process, charged toner is caused to adhere to the electrostatic charge image. After the adhered toner has been transferred onto a transfer belt as a toner image, the toner image on the transfer belt is transferred onto a recording medium (for example, paper). The toner is subsequently fixed to the recording medium through heating. As a result of the above process, an image is formed on the recording medium. A full-color image can for example be formed by superposing toner images of four different colors: black, yellow, magenta, and cyan.

The following explains the composition of the toner (in particular, the toner particles) according to the present embodiment with reference to FIG. 1. FIG. 1 illustrates a toner particle 10 included in the toner according to the present embodiment.

As illustrated in FIG. 1, the toner particle 10 includes a core 11, a shell layer (capsule layer) 12 disposed over the surface of the core 11, and an external additive 13. Herein, particles that are yet to be subjected to external addition (i.e., toner particles that do not include an adhered external additive) are referred to as toner mother particles.

The core 11 contains a binder resin 11a and internal additives 11b (for example, a colorant and a releasing agent). The shell layer 12 coats the core 11. The external additive 13 adheres to the surface of the shell layer 12. Note that the internal additives 11b and the external additive 13 may be omitted if such additives are unnecessary. Also, a plurality of shell layers 12 may be layered over the surface of the core 11.

In the toner according to the present embodiment, a Young's modulus of the core 11 and a Young's modulus of the shell layer 12, as measured using a scanning probe microscope (SPM) while raising the temperature of a cantilever of the SPM, satisfy conditions (1) and (2) shown below. Note that X1 denotes a proportion of change of the Young's modulus of the shell layer 12 upon raising the cantilever temperature from 30° C. to 50° C. X2 denotes a proportion of change of the Young's modulus of the core 11 upon raising the cantilever temperature from 30° C. to 50° C. Y1 denotes a proportion of change of the Young's modulus of the shell layer 12 upon raising the cantilever temperature from 50° C. to 70° C. Y2 denotes a proportion of change of the Young's modulus of the core 11 upon raising the cantilever temperature from 50° C. to 70° C.

(1) X2 is greater than X1 and X2/X1 is at least 2.0 and no greater than 5.0.

(2) Y2/Y1 is at least 4.0 and no greater than 7.0.

The toner according to the present embodiment includes toner particles 10 that satisfy conditions (1) and (2) (herein referred to as toner particles 10 according to the present embodiment). The toner including the toner particles 10 according to the present embodiment has excellent properties in terms of both high-temperature preservability and low-temperature fixability (refer to Tables 2 and 3 explained further below). Among toner particles included in the toner, preferably at least 80% by number are toner particles 10 according to the present embodiment, more preferably at least 90% by number are toner particles 10 according to the present

embodiment, and particularly preferably 100% by number are toner particles **10** according to the present embodiment.

The cores **11** are preferably anionic. A material of the shell layers **12** (herein referred to as a shell material) is preferably cationic. As a result of the cores **11** being anionic, the cationic shell material can be attracted toward the surface of the cores **11** during formation of the shell layers **12**. More specifically, it is thought that the shell material which has a positive charge in an aqueous medium is attracted toward the cores **11** which have a negative charge in the aqueous medium and the shell layers **12** are formed over the surface of the cores **11**, for example, by in-situ polymerization. As a consequence of the shell material being attracted toward the cores **11**, it is thought that the shell layers **12** can be readily formed in a uniform manner over the surface of the cores **11** without needing to use a dispersant in order to achieve a high degree of dispersion of the cores **11** in the aqueous medium.

The cores **11** having a triboelectric charge of no greater than  $-10\mu\text{C/g}$  is an indicator that the cores **11** are anionic. The cores **11** having a negative zeta potential (i.e., less than 0 V) measured in an aqueous medium adjusted to pH 4 (herein referred to simply as a zeta potential at pH 4) is also an indicator that the cores **11** are anionic. In order that the cores **11** and the shell layers **12** bond more strongly to one another, the cores **11** preferably have a zeta potential at pH 4 of less than 0 V and the toner particles **10** preferably have a zeta potential at pH 4 of greater than 0 V. Note that pH 4 corresponds to the pH of the aqueous medium during formation of the shell layers **12** in the present embodiment.

Examples of methods for measuring the zeta potential include an electrophoresis method, an ultrasound method, and an electric sonic amplitude (ESA) method.

The electrophoresis method involves applying an electrical field to a liquid dispersion of particles, thereby causing electrophoresis of charged particles in the dispersion, and measuring the zeta potential based on the rate of electrophoresis. An example of the electrophoresis method is laser Doppler electrophoresis in which migrating particles are irradiated with laser light and the rate of electrophoresis of the particles is calculated from an amount of Doppler shift of scattered light that is obtained. Advantages of laser Doppler electrophoresis are a lack of necessity for particle concentration in the dispersion to be high, a low number of parameters being necessary for calculating the zeta potential, and a good degree of sensitivity in detection of the rate of electrophoresis.

The ultrasound method involves irradiating a liquid dispersion of particles with ultrasound, thereby causing vibration of electrically charged particles in the dispersion, and measuring the zeta potential based on an electric potential difference that arises due to the vibration.

The ESA method involves applying a high frequency voltage to a liquid dispersion of particles, thereby causing electrically charged particles in the dispersion to vibrate and generate ultrasound. The zeta potential is then measured based on the magnitude (intensity) of the ultrasound.

An advantage of the ultrasound method and the ESA method is that the zeta potential can be measured to a good degree of sensitivity even when particle concentration of the dispersion is high (for example, exceeding 20% by mass).

The amount of dispersant used during formation of the shell layers **12** is preferably no greater than 1 part by mass relative to 100 parts by mass of the cores **11**. As a result of the amount of the dispersant being within the aforementioned range, the burden of effluent treatment can be reduced. The amount of water used during a washing process can also be reduced. Also, the total organic carbon (TOC) concentration of effluent discharged during manufacture of the toner par-

ticles **10** can be restricted to a low level of no greater than 15 mg/L without diluting the effluent.

The organic component (for example, unreacted monomer, prepolymer, or dispersant) of an effluent can be measured by measuring biochemical oxygen demand (BOD), chemical oxygen demand (COD), or TOC concentration. Among the above methods of measuring organic content, measurement based on the TOC concentration enables reliable measurement of all organic substances. Also, by measuring the TOC concentration, the amount of organic component in the effluent (i.e., filtrates after washing) which does not contribute to capsulation (i.e., formation of the shell layers **12**) can be determined.

The following explains, in order, the cores **11** (binder resin **11a** and internal additives **11b**), the shell layers **12**, and the external additive **13**. Note that herein the term "(meth) acrylic" is used as a generic term for both acrylic and methacrylic.

#### [Cores]

The cores **11** contain the binder resin **11a**. The cores **11** may optionally contain one or more internal additives **11b** (a colorant, a releasing agent, a charge control agent, and a magnetic powder). However, non-essential components (for example, the colorant, the releasing agent, the charge control agent, and the magnetic powder) may be omitted in accordance with intended use of the toner.

#### [Binder Resin (Cores)]

The binder resin **11a** constitutes a large proportion (for example, at least 85% by mass) of components contained in the cores **11**. Therefore, the polarity of the binder resin **11a** has a significant influence on the overall polarity of the cores **11**. For example, when the binder resin **11a** has an ester group, a hydroxyl group, an ether group, an acid group, or a methyl group, the cores **11** tend to be anionic. On the other hand, when the binder resin **11a** for example has an amino group, an amine, or an amide group, the cores **11** tend to be cationic.

In order that the binder resin **11a** is strongly anionic, the binder resin **11a** preferably has a hydroxyl value (measured according to Japanese Industrial Standard (JIS) K-0070) and an acid value (measured according to JIS K-0070) that are each at least 10 mg KOH/g, and more preferably at least 20 mg KOH/g.

The glass transition point ( $T_g$ ) of the binder resin **11a** is preferably no greater than a curing initiation temperature of the shell material. As a result of the binder resin **11a** having a  $T_g$  such as described above, the toner can be fixed more readily at low temperatures, even during high speed fixing. A curing reaction to form a melamine resin in an aqueous medium (i.e., a reaction of melamine monomers) typically occurs rapidly at 50° C. or higher when the aqueous medium has an acidic pH of 4. In a composition in which the shell layers **12** contain a melamine resin,  $T_g$  of the binder resin **11a** is preferably close to a reaction temperature (50° C.) of melamine monomers. More specifically,  $T_g$  of the binder resin **11a** is preferably at least 20° C. and no greater than 55° C. During manufacture of a toner having a composition such as described above, shell layers **12** that are hard and thin can be easily formed over the surface of the cores **11** in an aqueous medium while controlling shape of particles through surface tension of the binder resin **11a**.

The binder resin **11a** preferably has a softening point ( $T_m$ ) of no greater than 105° C., and more preferably no greater than 95° C. As a result of  $T_m$  of the binder resin **11a** being no greater than 105° C. (more preferably no greater than 95° C.), it is thought that the toner can be more readily fixed at low temperatures, even during high speed fixing. Also, as a result

of T<sub>m</sub> of the binder resin **11a** being no greater than 105° C. (more preferably no greater than 95° C.), the cores **11** are partially softened while a curing reaction of the shell layers **12** occurs during formation of the shell layers **12** on the surface of the cores **11** in an aqueous medium, thereby causing spheroidizing due to surface tension. Note that T<sub>m</sub> of the binder resin **11a** can be adjusted by combining, as the binder resin **11a**, a plurality of resins that each have a different T<sub>m</sub>.

The following explains a method of reading T<sub>g</sub> of the binder resin **11a** from a heat absorption curve with reference to FIG. 2. FIG. 2 is a graph illustrating an example of a heat absorption curve.

The glass transition point (T<sub>g</sub>) of the binder resin **11a** can be measured according to the method described below. A heat absorption curve of the binder resin **11a** can be plotted using a differential scanning calorimeter (for example, a DSC-6220 produced by Seiko Instruments Inc.). FIG. 2 illustrates an example of the heat absorption curve which is plotted. The glass transition point (T<sub>g</sub>) of the binder resin **11a** can be calculated from the heat absorption curve that is plotted (more specifically, from a point of change of specific heat of the binder resin **11a**).

The following explains a method of reading T<sub>m</sub> of the binder resin **11a** from an S-shaped curve with reference to FIG. 3. FIG. 3 is a graph illustrating an example of an S-shaped curve.

The softening point (T<sub>m</sub>) of the binder resin **11a** can be measured according to the method described below. The softening point (T<sub>m</sub>) of the binder resin **11a** can be measured using a capillary rheometer (for example, a CFT-500D produced by Shimadzu Corporation). For example, the binder resin **11a** (measurement sample) is placed in the capillary rheometer and melt-flow of the measurement sample is caused under specific conditions in order to plot an S-shaped curve of stroke (mm)/temperature (° C.). The softening point (T<sub>m</sub>) of the binder resin **11a** can be read from the S-shaped curve that is plotted. In FIG. 3, S<sub>1</sub> indicates a maximum stroke value and S<sub>2</sub> indicates a base line stroke value at low temperatures. T<sub>m</sub> of the measurement sample is equivalent to a temperature along the S-shaped curve at which the stroke value is (S<sub>1</sub>+S<sub>2</sub>)/2.

The following continues explanation of the binder resin **11a** shown in FIG. 1. The binder resin **11a** preferably has a functional group such as an ester group, a hydroxyl group, an ether group, an acid group, a methyl group, or a carboxyl group in molecules thereof, and more preferably has either or both of a hydroxyl group and a carboxyl group in molecules thereof. As a result of the cores **11** (binder resin **11a**) having a functional group such as described above, the cores **11** readily react with the shell material (for example, methylol melamine) to form chemical bonds. Formation of chemical bonds ensures that the cores **11** are strongly bound to the shell layers **12**.

The binder resin **11a** is preferably a thermoplastic resin. Preferable examples of thermoplastic resins that can be used as the binder resin **11a** include styrene-based resins, acrylic-based resins, styrene-acrylic-based resins, polyethylene-based resins, polypropylene-based resins, vinyl chloride-based resins, polyester resins, polyamide resins, urethane resins, polyvinyl alcohol-based resins, vinyl ether-based resins, N-vinyl-based resins, and styrene-butadiene-based resins. Among the resins listed above, styrene-acrylic-based resins and polyester resins are preferable in terms of improving colorant dispersibility in the toner, chargeability of the toner, and fixability of the toner to a recording medium.

#### (Styrene-Acrylic-Based Resins)

A styrene-acrylic-based resin is a copolymer of a styrene-based monomer and an acrylic-based monomer.

Preferable examples of styrene-based monomers that can be used in preparation of the styrene-acrylic-based resin (binder resin **11a**) include styrene,  $\alpha$ -methylstyrene, p-hydroxystyrene, m-hydroxystyrene, vinyltoluene,  $\alpha$ -chlorostyrene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene, and p-ethylstyrene.

Preferable examples of acrylic-based monomers that can be used in preparation of the styrene-acrylic-based resin (binder resin **11a**) include (meth)acrylic acid, alkyl (meth)acrylates, and hydroxyalkyl (meth)acrylates. Specific examples of preferable alkyl(meth)acrylates include methyl (meth)acrylate, ethyl(meth)acrylate, n-propyl(meth)acrylate, iso-propyl(meth)acrylate, n-butyl(meth)acrylate, iso-butyl (meth)acrylate, and 2-ethylhexyl(meth)acrylate. Specific examples of preferable hydroxyalkyl(meth)acrylates include 2-hydroxyethyl(meth)acrylate, 3-hydroxypropyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, and 4-hydroxybutyl (meth)acrylate.

A hydroxyl group can be introduced into the styrene-acrylic-based resin by using a hydroxyl group-containing monomer (for example, p-hydroxystyrene, m-hydroxystyrene, or a hydroxyalkyl(meth)acrylate) during preparation of the styrene-acrylic-based resin. The hydroxyl value of the styrene-acrylic-based resin which is prepared can be adjusted through adjustment of the amount of the hydroxyl group-containing monomer used during preparation of the styrene-acrylic-based resin.

A carboxyl group can be introduced into the styrene-acrylic-based resin by using (meth)acrylic acid (monomer) during preparation of the styrene-acrylic-based resin. The acid value of the styrene-acrylic-based resin which is prepared can be adjusted through adjustment of the amount of the (meth)acrylic acid used during preparation of the styrene-acrylic-based resin.

In a composition in which the binder resin **11a** is a styrene-acrylic-based resin, the styrene-acrylic-based resin preferably has a number average molecular weight (M<sub>n</sub>) of at least 2,000 and no greater than 3,000 in order to improve strength of the cores **11** and fixability of the toner. Also, the styrene-acrylic-based resin preferably has a molecular weight distribution (i.e., a ratio M<sub>w</sub>/M<sub>n</sub> of mass average molecular weight (M<sub>w</sub>) relative to number average molecular weight (M<sub>n</sub>)) of at least 10 and no greater than 20. M<sub>n</sub> and M<sub>w</sub> of the styrene-acrylic-based resin can be measured by gel permeation chromatography.

#### (Polyester Resins)

The polyester resin used as the binder resin **11a** is for example prepared through condensation polymerization or condensation copolymerization of a di-, tri-, or higher-hydric alcohol and a di-, tri-, or higher-basic carboxylic acid.

In a composition in which the binder resin **11a** is a polyester resin, preferable examples of alcohols that can be used in preparation of the polyester resin include diols, bisphenols, and tri- or higher-hydric alcohols such as described below.

Specific examples of preferable diols that can be used in preparation of the polyester resin include ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol, 1,4-butenediol, 1,5-pentanediol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, dipropylene glycol, polyethylene glycol, polypropylene glycol, and polytetramethylene glycol.

Specific examples of preferable bisphenols that can be used in preparation of the polyester resin include bisphenol A,

hydrogenated bisphenol A, polyoxyethylenated bisphenol A, and polyoxypropylenated bisphenol A.

Specific examples of preferable tri- or higher-hydric alcohols that can be used in preparation of the polyester resin include sorbitol, 1,2,3,6-hexanetetraol, 1,4-sorbitan, pentaerythritol, dipentaerythritol, tripentaerythritol, 1,2,4-butanetriol, 1,2,5-pentanetriol, glycerol, diglycerol, 2-methylpropanetriol, 2-methyl-1,2,4-butanetriol, trimethylethane, trimethylolpropane, and 1,3,5-trihydroxymethylbenzene.

In a composition in which the binder resin **11a** is a polyester resin, preferable examples of carboxylic acids that can be used in preparation of the polyester resin include di-, tri-, and higher-basic carboxylic acids such as described below.

Specific examples of preferable di-basic carboxylic acids that can be used in preparation of the polyester resin include maleic acid, fumaric acid, citraconic acid, itaconic acid, glutaric acid, phthalic acid, isophthalic acid, terephthalic acid, cyclohexanedicarboxylic acid, adipic acid, sebacic acid, azelaic acid, malonic acid, succinic acid, alkyl succinic acids (more specifically, n-butylsuccinic acid, isobutylsuccinic acid, n-octylsuccinic acid, n-dodecylsuccinic acid, and isododecylsuccinic acid), and alkenyl succinic acids (more specifically, n-butenylsuccinic acid, isobutenylsuccinic acid, n-octenylsuccinic acid, n-dodecenylsuccinic acid, and isododecenylsuccinic acid).

Specific examples of tri- or higher-basic carboxylic acids that can be used in preparation of the polyester resin include 1,2,4-benzenetricarboxylic acid (trimellitic acid), 1,2,5-benzenetricarboxylic acid, 2,5,7-naphthalenetricarboxylic acid, 1,2,4-naphthalenetricarboxylic acid, 1,2,4-butanetricarboxylic acid, 1,2,5-hexanetricarboxylic acid, 1,3-dicarboxyl-2-methyl-2-methylenecarboxypropane, 1,2,4-cyclohexanetricarboxylic acid, tetra(methylenecarboxyl)methane, 1,2,7,8-octanetetracarboxylic acid, pyromellitic acid, and EMPOL trimer acid.

Alternatively, an ester-forming derivative (acid halide, acid anhydride, or lower alkyl ester) of any of the di-, tri-, or higher-basic carboxylic acids listed above may be used. Herein, the term lower alkyl refers to an alkyl group having 1 to 6 carbon atoms.

The acid value and the hydroxyl value of the polyester resin can be adjusted through adjustment of the amount of the di-, tri-, or higher-hydric alcohol and the amount of the di-, tri-, or higher-basic carboxylic acid used during preparation of the polyester resin. Increasing the molecular weight of the polyester resin tends to decrease the acid value and the hydroxyl value of the polyester resin.

In a composition in which the binder resin **11a** is a polyester resin, the polyester resin preferably has a number average molecular weight (Mn) of at least 1,200 and no greater than 2,000 in order to improve strength of the cores **11** and fixability of the toner. Also, the polyester resin preferably has a molecular weight distribution (i.e., a ratio Mw/Mn of mass average molecular weight (Mw) relative to number average molecular weight (Mn)) of at least 9 and no greater than 20. Mn and Mw of the polyester resin can be measured by gel permeation chromatography.

#### [Colorant (Cores)]

The cores **11** may optionally contain a colorant as an internal additive **11b**. The colorant can be a commonly known pigment or dye that matches the color of the toner. The amount of the colorant is preferably at least 1 part by mass and no greater than 20 parts by mass relative to 100 parts by mass of the binder resin **11a**, and more preferably at least 3 parts by mass and no greater than 10 parts by mass.

#### (Black Colorants)

The cores **11** may optionally contain a black colorant. The black colorant is for example carbon black. Alternatively, a colorant may be used that has been adjusted to a black color using colorants such as a yellow colorant, a magenta colorant, and a cyan colorant.

#### (Non-Black Colorants)

The cores **11** may optionally contain a non-black colorant such as a yellow colorant, a magenta colorant, or a cyan colorant.

Examples of yellow colorants include condensed azo compounds, isoindolinone compounds, anthraquinone compounds, azo metal complexes, methine compounds, and arylamide compounds. Specific examples of preferable yellow colorants include C.I. Pigment Yellow (3, 12, 13, 14, 15, 17, 62, 74, 83, 93, 94, 95, 97, 109, 110, 111, 120, 127, 128, 129, 147, 151, 154, 155, 168, 174, 175, 176, 180, 181, 191, and 194), Naphthol Yellow S, Hansa Yellow G, and C.I. Vat Yellow.

Examples of magenta colorants include condensed azo compounds, diketopyrrolopyrrole compounds, anthraquinone compounds, quinacridone compounds, basic dye lake compounds, naphthol compounds, benzimidazolone compounds, thioindigo compounds, and perylene compounds. Specific examples of preferable magenta colorants include C.I. Pigment Red (2, 3, 5, 6, 7, 19, 23, 48:2, 48:3, 48:4, 57:1, 81:1, 122, 144, 146, 150, 166, 169, 177, 184, 185, 202, 206, 220, 221, and 254).

Examples of cyan colorants include copper phthalocyanine compounds, copper phthalocyanine derivatives, anthraquinone compounds, and basic dye lake compounds. Specific examples of preferable cyan colorants include C.I. Pigment Blue (1, 7, 15, 15:1, 15:2, 15:3, 15:4, 60, 62, and 66), Phthalocyanine Blue, C.I. Vat Blue, and C.I. Acid Blue.

#### [Releasing Agent (Cores)]

The cores **11** may optionally contain a releasing agent as an internal additive **11b**. The releasing agent is for example used in order to improve fixability or offset resistance of the toner. In order to improve fixability or offset resistance of the toner, the amount of the releasing agent is preferably at least 1 part by mass and no greater than 30 parts by mass relative to 100 parts by mass of the binder resin **11a**, and more preferably at least 5 parts by mass and no greater than 20 parts by mass.

Examples of preferable releasing agents include: aliphatic hydrocarbon-based waxes such as low molecular weight polyethylene, low molecular weight polypropylene, polyolefin copolymer, polyolefin wax, microcrystalline wax, paraffin wax, and Fischer-Tropsch wax; oxides of aliphatic hydrocarbon-based waxes such as polyethylene oxide wax and block copolymer of polyethylene oxide wax; plant waxes such as candelilla wax, carnauba wax, Japan wax, jojoba wax, and rice wax; animal waxes such as beeswax, lanolin, and spermaceti; mineral waxes such as ozocerite, ceresin, and petrolatum; waxes having a fatty acid ester as major component such as montanic acid ester wax and castor wax; and waxes in which a part or all of a fatty acid ester has been deoxidized such as deoxidized carnauba wax.

Note that compatibility between the releasing agent and the binder resin **11a** tends to be poor. Therefore, a compatibilizer having a functional group that is compatible with both the binder resin and the releasing agent is preferably used in accordance with necessity thereof.

#### [Charge Control Agent (Cores)]

The cores **11** may optionally contain a charge control agent as an internal additive **11b**. The charge control agent is for example used in order to improve charge stability or a charge rise characteristic of the toner. The charge rise characteristic



is an indicator of whether or not the toner can be charged to a specific charge level in a short period of time.

#### [Magnetic Powder (Cores)]

The cores **11** may optionally contain a magnetic powder as an internal additive **11b**. Preferable examples of a material of the magnetic powder include iron (more specifically, ferrite and magnetite), ferromagnetic metals (more specifically, cobalt and nickel), alloys containing either or both of iron and a ferromagnetic metal, ferromagnetic alloys subjected to ferromagnetization such as heat treatment, and chromium dioxide.

The magnetic powder is preferably subjected to surface treatment in order to inhibit elution of iron ions from the magnetic powder. In a situation in which the shell layers **12** are formed on the surface of the cores **11** under acidic conditions, elution of iron ions to the surface of the cores **11** causes the cores **11** to adhere to one another more readily. Inhibiting elution of iron ions from the magnetic powder thereby inhibits the cores **11** from adhering to one another.

#### [Shell Layers]

The shell layers **12** contain a unit derived from a thermoplastic resin and a unit derived from a monomer or prepolymer of a thermosetting resin. For example, the unit derived from the thermoplastic resin is cross-linked by the unit derived from the monomer or prepolymer of the thermosetting resin. The shell layers **12** such as described above are thought to have suitable flexibility due to the thermoplastic resin and suitable mechanical strength due to the three-dimensional cross-linking structure formed by the monomer or prepolymer of the thermosetting resin. Therefore, a toner including the toner particles **10** that each include a shell layer **12** such as described above is considered to have excellent high-temperature preservability and low-temperature fixability. More specifically, the shell layers **12** are not readily ruptured during storage or transport of the toner. On the other hand, during fixing of the toner, the shell layers **12** are readily ruptured due to application of heat and pressure, and softening or melting of the cores **11** (for example, the binder resin **11a**) proceeds rapidly. Therefore, the toner can be fixed to a recording medium at low temperatures. In order to improve high-temperature preservability and low-temperature fixability of the toner, the shell layers **12** are preferably essentially composed of the unit derived from the thermoplastic resin and the unit derived from the monomer or prepolymer of the thermosetting resin.

Note that the unit derived from the thermoplastic resin (herein referred to as a thermoplastic unit) may be a unit that is modified, for example by introduction of a functional group, oxidation, reduction, or substitution of atoms, without drastically changing the structure or properties of the base thermoplastic resin. Also, the unit derived from the monomer or prepolymer of the thermosetting resin (herein referred to as a thermosetting unit) may be a unit that is modified, for example by introduction of a functional group, oxidation, reduction, or substitution of atoms, without drastically changing the structure or properties of the base monomer or prepolymer of the thermosetting resin.

During formation of the shell layers **12** over the surface of the cores **11** through in-situ polymerization, the thermoplastic unit is taken into the shell layers **12** (condensation films) at the same time as the polymerization, enabling the shell layers **12** to be readily formed over the surface of the cores **11** in a uniform manner.

The thermosetting resin is readily chargeable to a strong positive charge. In the toner according to the present embodiment, as a result of the shell layers **12** containing the thermoplastic unit in addition to the thermosetting unit, the charge of

the toner can be easily adjusted to within a desired range. Note that the shell layers **12** may for example optionally contain a positively chargeable charge control agent.

In order to inhibit dissolution of the binder resin **11a** or elution of the releasing agent during formation of the shell layers **12**, the formation of the shell layers **12** is preferably carried out in an aqueous medium. Therefore, the shell material is preferably water-soluble.

The thermoplastic resin relating to the thermoplastic unit preferably has a functional group that readily reacts with a functional group of the thermosetting resin (for example, a methylol group or an amino group). For example, the thermoplastic resin relating to the thermoplastic unit preferably has a reactive functional group containing activated hydrogen (for example, a hydroxyl group, a carboxyl group, or an amino group). The amino group may be present in the thermoplastic resin in the form of a carbamoyl group ( $-\text{CONH}_2$ ). The thermoplastic resin relating to the thermoplastic unit preferably has a carbodiimide group, an oxazoline group, or a glycidyl group. For example, the shell layers **12** may be formed using a cross-linking agent that has a carbodiimide group.

The thermoplastic unit preferably contains an acrylic component and more preferably contains a reactive acrylate. The thermoplastic unit containing the acrylic component is thought to readily react with the thermosetting resin, thereby enabling improved film quality of the shell layers **12**. It is particularly preferable that the thermoplastic unit contains 2HEMA (2-hydroxyethyl methacrylate).

Specific examples of the thermoplastic resin relating to the thermoplastic unit include acrylic-based resins, styrene-acrylic-based copolymers, silicone-acrylic-based graft copolymers, urethane resins, polyester resins, and ethylene vinyl alcohol copolymers. The thermoplastic resin relating to the thermoplastic unit is preferably an acrylic-based resin, a styrene-acrylic-based copolymer, or a silicone-acrylic-based graft copolymer, with an acrylic-based resin being particularly preferable. Inclusion of a silicone-acrylic-based graft copolymer in the shell layers **12** can improve water resistance of the shell layers **12**.

Among the above-listed thermoplastic resins relating to the thermoplastic unit, preferable examples of thermoplastic resins that are water-soluble include polyvinyl alcohol-based resins, polyvinylpyrrolidone, carboxymethyl cellulose (or a derivative thereof), sodium polyacrylate, polyacrylamide, polyethylenimine, and polyethylene oxide. Also, the thermoplastic resin is preferably a water-soluble resin derived from a monomer having a polar functional group (for example, a glycol, a carboxylic acid, or maleic acid). The thermoplastic resin having a polar functional group has a high reactivity.

Examples of acrylic-based monomers that can be used in preparation of the acrylic-based resin include: alkyl(meth)acrylates such as methyl(meth)acrylate, ethyl(meth)acrylate, n-propyl(meth)acrylate, and n-butyl(meth)acrylate; aryl(meth)acrylates such as phenyl(meth)acrylate; hydroxyalkyl(meth)acrylates such as 2-hydroxyethyl(meth)acrylate, 3-hydroxypropyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, and 4-hydroxybutyl(meth)acrylate; (meth)acrylamide; ethylene oxide adduct of (meth)acrylic acid; and alkyl ethers, such as methyl ether, ethyl ether, n-propyl ether, and n-butyl ether, of ethylene oxide adducts of (meth)acrylic acid esters.

The thermoplastic unit may be formed using a water-soluble resin, using a liquid dispersion of oily fine particles dispersed in water as a suspension, or using a silane coupling agent.

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The thermosetting resin relating to the thermosetting unit is for example preferably a melamine resin, a urea resin, a sulfonamide resin, a glyoxal resin, a guanamine resin, an aniline resin, or a derivative of any of the aforementioned resins. A polyimide resin contains nitrogen in a molecular framework thereof. As a consequence, shell layers 12 containing a polyimide resin tend to be strongly cationic. Preferable examples of polyimide resins that may be contained in the shell layers 12 include maleimide-based polymers and bismaleimide-based polymers (for example, amino-bismaleimide polymers and bismaleimide triazine polymers).

In particular, the thermosetting resin relating to the thermosetting unit is preferably a resin generated by polycondensation of an aldehyde (for example, formaldehyde) and a compound containing an amino group. Note that a melamine resin is a polycondensate of melamine and formaldehyde. A urea resin is a polycondensate of urea and formaldehyde. A glyoxal resin is a polycondensate of formaldehyde and a reaction product of glyoxal and urea.

Inclusion of nitrogen in the thermosetting resin enables the thermosetting resin to perform a function of cross-link curing more effectively. In order that the thermosetting resin has a high reactivity, the amount of nitrogen contained therein is preferably adjusted to be at least 40% by mass and no greater than 55% by mass in the case of a melamine resin, approximately 40% by mass in the case of a urea resin, and approximately 15% by mass in the case of a glyoxal resin.

The thermosetting unit can be prepared using at least one monomer (shell material) selected from the group consisting of methylol melamine, melamine, methylol urea (for example, dimethylol dihydroxyethyleneurea), urea, benzoguanamine, acetoguanamine, and spiroguanamine. The shell material preferably dissolves or disperses in water. A curing agent or a reaction accelerator may also be used in formation of the shell layers 12.

The shell layers 12 preferably have a thickness of at least 1 nm and no greater than 20 nm, and more preferably at least 1 nm and no greater than 10 nm.

As a result of the thickness of the shell layers 12 being no greater than 20 nm, the shell layers 12 are readily ruptured due to application of heat and pressure during fixing of the toner to a recording medium. Therefore, softening or melting of the binder resin 11a and the releasing agent contained in the cores 11 proceeds rapidly, enabling fixing of the toner to the recording medium at low temperatures. Also, as a result of the thickness of the shell layers 12 being no greater than 20 nm, chargeability of the shell layers 12 can be restricted from becoming excessively strong. Therefore, an image having high image quality can be more easily formed using the toner.

On the other hand, as a result of the thickness of the shell layers 12 being at least 1 nm, the shell layers 12 tend to have sufficient strength. Therefore, rupturing of the shell layers 12 during transport, for example due to impact, can be inhibited, thereby improving preservability of the toner.

The thickness of the shell layers 12 of the target toner particles 10 can be measured by analyzing cross-sectional transmission electron microscopy (TEM) images of the toner particles 10 using commercially available image analysis software (for example, WinROOF produced by Mitani Corporation). Note that if the thickness of the shell layer 12 is not uniform for a single toner particle, the thickness of the shell layer 12 is measured at each of four locations that are approximately evenly spaced and the arithmetic mean of the four measured values is determined to be an evaluation value (thickness of shell layer 12) for the toner particle. More specifically, the four measurement locations are determined by drawing two straight lines that intersect at right angles at

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approximately the center of the cross-section and by determining four locations at which the straight lines and the shell layer intersect to be the measurement locations.

The shell layers 12 may have fractures therein (i.e., portions having low mechanical strength). The fractures can be formed by causing localized defects to occur in the shell layers 12. Formation of the fractures in the shell layers 12 enables the shell layers 12 to be ruptured more readily. Therefore, the toner can be fixed to a recording medium at low temperatures. Any appropriate number of fractures may be present in the shell layers 12.

[External Additive]

The external additive 13 is for example used in order to improve fluidity or handleability of the toner. In order to improve fluidity or handleability of the toner, the amount of the external additive 13 is preferably at least 0.5 parts by mass and no greater than 10 parts by mass relative to 100 parts by mass of the toner mother particles, and more preferably at least 2 parts by mass and no greater than 5 parts by mass.

The external additive 13 is for example composed of particles of silica or particles of a metal oxide (more specifically, alumina, titanium oxide, magnesium oxide, zinc oxide, strontium titanate, or barium titanate).

In order to improve fluidity or handleability of the toner, the external additive 13 preferably has a number average primary particle diameter of at least 0.01  $\mu\text{m}$  and no greater than 1.0  $\mu\text{m}$ .

[Toner Manufacturing Method]

The following explains a toner manufacturing method according to the present embodiment. The toner manufacturing method according to the present embodiment includes forming a plurality of cores 11. Next, at least the cores 11, a material for forming a thermoplastic unit, and a material for forming a thermosetting unit are added to a liquid. Next, shell layers 12 containing the thermoplastic unit and the thermosetting unit are formed over the surface of the cores 11 in the liquid. The Young's modulus of the shell layers 12 that are formed on the surface of the cores 11 is adjusted based on a ratio of the additive amount of the material for forming the thermosetting unit relative to the additive amount of the material for forming the thermoplastic unit.

FIG. 4 indicates a relationship between Young's modulus and temperature (i.e., a hardness characteristic) for a thermoplastic resin, a thermosetting resin, and a resin containing both a thermoplastic unit and a thermosetting unit (herein referred to as a composite resin). In FIG. 4, curve L10 indicates the hardness characteristic of the composite resin (more specifically, the shell layers 12 included in the toner according to the present embodiment). Curve L11 indicates the hardness characteristic of the thermoplastic resin (more specifically, the cores 11 included in the toner according to the present embodiment). Curve L12 indicates a hardness characteristic of the thermosetting resin (more specifically, shell layers included in another capsule toner which are only composed of the thermosetting resin). The Young's modulus was measured using an SPM. The temperature shown in FIG. 4 corresponds to the cantilever temperature of the SPM.

As illustrated in FIG. 4, the composite resin has a hardness characteristic that is intermediate between the hardness characteristic of the thermoplastic resin and the hardness characteristic of the thermosetting resin. As a proportion of the thermoplastic unit contained in the composite resin increases, the hardness characteristic of the composite resin tends to more closely resemble the hardness characteristic of the thermoplastic resin. On the other hand, as a proportion of the thermosetting unit contained in the composite resin increases, the hardness characteristic of the composite resin tends to

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more closely resemble the hardness characteristic of the thermosetting resin. Therefore, the hardness characteristic (Young's modulus) of the composite resin can be adjusted by adjusting the ratio of the thermoplastic unit and the thermosetting unit contained in the composite resin.

In the toner manufacturing method relating to the present embodiment, the Young's modulus of the shell layers **12** is adjusted based on a ratio of an additive amount of a material for forming a thermoplastic unit and an additive amount of a material for forming a thermosetting unit (i.e., additive amount of material for forming thermosetting unit/additive amount of material for forming thermoplastic unit). The toner manufacturing method according to the present embodiment facilitates manufacture of a toner having good high-temperature preservability and low-temperature fixability.

The following further explains the toner manufacturing method according to the present embodiment based on a specific example. For example, first ion exchanged water is prepared as the aforementioned liquid. Next, the pH of the liquid is adjusted using, for example, hydrochloric acid. A shell material (i.e., a material for forming a thermoplastic unit and a material for forming a thermosetting unit) is subsequently added to the liquid. The shell material is dissolved in the liquid to obtain a solution. An appropriate additive amount of the shell material can be calculated based on the specific surface area of the cores **11**. Addition of the shell material is for example performed at room temperature. The temperature of the liquid can be used to control the molecular weight of the shell layers **12** (polycondensation films).

Next, the cores **11** are added to the resultant solution and the solution is heated while stirring. For example, the solution may be heated to 70° C. over 30 minutes at a heating rate of 1° C./minute. As a result, the shell material adheres to the surface of the cores **11** and hardens while adhered thereto by undergoing a polymerization reaction. The cores **11** can for example be prepared according to a dry pulverization process, a dissolution-suspension granulation process, or a high-pressure emulsification process.

The cores **11** transform in terms of shape if the temperature of the solution becomes equal to or greater than the glass transition point (T<sub>g</sub>) of the cores **11**. For example, in a situation in which T<sub>g</sub> of the binder resin **11a** of the cores **11** is 45° C. and the thermosetting unit contained in the shell layers **12** is a unit derived from a monomer or prepolymer of a melamine resin, heating of the solution to approximately 50° C. causes a curing reaction of the shell material (specifically, the material for forming the thermosetting unit) to proceed rapidly and the cores **11** to transform in terms of shape. When the shell material is caused to react at high temperatures, hard films (shell layers **12**) tend to be formed. Also, the cores **11** transform more readily in terms of shape with increasing temperature of the liquid, thereby tending to yield toner mother particles that are more spherical. Therefore, preferably the reaction temperature is determined in order to obtain toner mother particles of a desired shape.

Next, the solution is neutralized. The neutralized solution is subsequently cooled. Once cooled, the solution is filtered. Through the above process, the toner mother particles are separated from the liquid (solid-liquid separation). Next, the toner mother particles that have been separated are dried. An external additive **13** is subsequently caused to adhere to the surface of the toner mother particles. The above completes the manufacture of a toner including a large number of toner particles **10**.

The toner manufacturing method described above can be altered in accordance with intended composition, properties, or the like of the toner. For example, the cores **11** may be

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added to the solvent prior to dissolving the shell material in the solvent, or the shell material and the cores **11** may be added to the solvent at the same time. Also, the shell material may be added to the solvent as a single addition or may be divided up and added to the solvent as a plurality of additions. The shell layers **12** may be formed according to any appropriate process. For example, the shell layers **12** may be formed according to an in-situ polymerization process, an in-liquid curing film coating process, or a coacervation process. Also, the toner may be sifted after external addition. Note that non-essential processes may alternatively be omitted. In a process in which an external additive is not caused to adhere to the surface of the toner mother particles (i.e., a process in which external addition is omitted), the toner mother particles are equivalent to the toner particles. The material for forming the cores (herein referred to as a core material) and the shell material are not limited to the compounds (for example, resin-forming monomers) listed above. For example, alternatively a derivative of any of the compounds listed above may be used as the core material or the shell material in accordance with necessity thereof. Preferably a large number of the toner particles **10** are formed at the same time in order that the toner can be manufactured efficiently.

## EXAMPLES

The following explains Examples of the present disclosure. Table 1 shows details of toners A-G (electrostatic charge image developing toners).

TABLE 1

| Toner   | Shell material (relative additive amounts) |                     | Shell layer thickness (nm) |
|---------|--|---------------------|----------------------------|
|         | Thermosetting resin                        | Thermoplastic resin |                            |
| Toner A | 5  | 5                   | 10                         |
| Toner B | 8  | 2                   | 10                         |
| Toner C | 2  | 8                   | 10                         |
| Toner D | 5  | 5                   | 10                         |
| Toner E | 10   | 0                   | 10                         |
| Toner F | 0  | 10                  | 50                         |
| Toner G | 5  | 5                   | 10                         |

The following explains, in order, a preparation method, an evaluation method, and evaluation results for each of toners A-G. Note that unless specifically stated, the evaluation results (for example, values indicating shape and physical properties) of the toners are number averages of values measured with respect to an appropriate number of particles.

[Preparation Method of Toner A]

(Core Preparation)

The following explains a procedure for preparing cores in the preparation method of toner A.

In the preparation method of toner A, the cores are prepared according to a pulverization and classification process. In the process of preparing the cores, 1,245 g of terephthalic acid, 1,245 g of isophthalic acid, 1,248 g of bisphenol A ethylene oxide adduct, and 744 g of ethylene glycol were added to a four-necked flask having a capacity of 5 L. The contents of the flask were caused to react for four hours at 220° C. under standard pressure. Next, 0.875 g of antimony trioxide, 0.548 g of triphenyl phosphate, and 0.102 g of tetrabutyl titanate were added to the flask. The internal pressure of the flask was subsequently reduced to 0.3 mmHg and the contents of the flask were caused to undergo a polycondensation reaction at 250° C.

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Next, 30.0 g of trimellitic acid was added to the flask as a cross-linking agent. The contents of the flask were subsequently caused to react for one hour at 240° C. under standard pressure in an inert atmosphere. The above yielded a polyester resin having an Mn of 1,460, a hydroxyl value of 22.8 mg KOH/g (measured according to JIS K-0070), an acid value of 16.8 mg KOH/g (measured according to JIS K-0070), a Tm of 100.5° C., and a Tg of 53.8° C. The polyester resin had a ratio Mw/Mn (molecular weight distribution) of 12.7. Mw and Mn of the polyester resin were measured using a gel permeation chromatography (GPC) apparatus (HLC-8220GPC produced by Tosoh Corporation). Tm of the polyester resin was measured using a capillary rheometer (CFT-500D produced by Shimadzu Corporation). Tg of the polyester resin was measured using a differential scanning calorimeter (DSC-6220 produced by Seiko Instruments Inc.).

Next, 100 parts by mass of the polyester resin, 5 parts by mass of a colorant, and 5 parts by mass of a releasing agent were dry-mixed using a mixer (FM mixer produced by Nippon Coke & Engineering Co., Ltd.). C.I. Pigment Blue 15:3 (phthalocyanine pigment) was used as the colorant. An ester wax (WEP-3 produced by NOF Corporation) was used as the releasing agent.

The resultant mixture was kneaded using a twin screw extruder (PCM-30 produced by Ikegai Corp.). Next, the kneaded product (chip) was pulverized using a mechanical pulverizer (Turbo Mill produced by Freund-Turbo Corporation) set to a particle diameter of 5.6 µm. The pulverized product was classified using a classifier (Elbow Jet produced by Nittetsu Mining Co., Ltd.). Through the above process, cores having a median diameter (volume distribution standard) of 6.0 µm were obtained.

The cores that were obtained had a roundness of 0.93 (number average for 3,000 cores). The roundness was measured using a flow particle imaging analyzer (FPIA (registered Japanese trademark) 3000 manufactured by Sysmex Corporation).

The cores that were obtained had a Tg of 47° C. and a Tm of 90° C. Tg of the cores was measured using a differential scanning calorimeter (DSC-6220 produced by Seiko Instruments Inc.). Tm of the cores was measured using a capillary rheometer (CFT-500D produced by Shimadzu Corporation).

The cores that were obtained had a triboelectric charge of -20 µC/g. The triboelectric charge was measured with a standard carrier using a Q/m meter (Model 210HS-2A produced by Trek, Inc.). More specifically, the cores and a standard carrier N-01 (standard carrier for negative-charging toner) provided by The Imaging Society of Japan were mixed for 30 minutes using a TURBULA mixer. The amount of the cores was 7% by mass relative to the standard carrier. After mixing, the triboelectric charge was measured using the Q/m meter.

The zeta potential of the cores in a dispersion adjusted to pH 4 was measured using a zeta potential and particle size distribution analyzer (DelsaNano HC manufactured by Beckman Coulter, Inc.). More specifically, 0.2 g of the cores, 80 g of ion exchanged water, and 20 g of 1% by mass concentration non-ionic surfactant (polyvinylpyrrolidone K-85 produced by Nippon Shokubai Co., Ltd.) were mixed using a magnetic stirrer to uniformly disperse the cores in liquid. Through the above, a dispersion of the cores was obtained. Next, the dispersion was adjusted to pH 4 through addition of dilute hydrochloric acid. The resultant pH 4 dispersion of the cores was used as a measurement sample. The zeta potential of the cores in the measurement sample was measured using the zeta potential and particle size distribution analyzer. The cores had

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a zeta potential of -15 mV at pH 4. The measured results for the triboelectric charge and the zeta potential clearly indicate that the cores were anionic.

(Shell Layer Formation)

The following explains a procedure for forming shell layers in the preparation method of toner A.

A three-necked flask having a capacity of 1 L and equipped with a thermometer and a stirring impeller was set up, and the internal temperature of the flask was maintained at 30° C. using a water bath. Next, 300 mL of ion exchanged water was added to the flask and the aqueous medium in the flask was adjusted to pH 4 through addition of dilute hydrochloric acid.

Next, 2 mL of an aqueous solution of hexamethylol melamine prepolymer (MIRBANE (registered Japanese trademark) resin SM-607 produced by Showa Denko K.K.; solid component concentration 80% by mass) and 2 mL of an aqueous solution of acrylamide resin (BECKAMINE (registered Japanese trademark) A-1 produced by DIC Corporation; solid component concentration 11% by mass) were added to the flask. The contents of the flask were subsequently stirred in order to dissolve the methylol melamine and the acrylamide resin in the aqueous medium. In the preparation method of toner A, the volume ratio of the additive amount of the material for forming the thermosetting unit (i.e., MIRBANE resin SM-607) and the additive amount of the material for forming the thermoplastic unit (i.e., BECKAMINE A-1) was 5:5 (=1:1).

Next, 300 g of the cores prepared according to the process described above were added to the flask and the contents of the flask were sufficiently stirred.

Next, 300 mL of ion exchanged water was added to the flask. The internal temperature of the flask was increased to 70° C. at a rate of 1° C./minute while stirring the contents of the flask and the internal temperature was then maintained at 70° C. for two hours. Through the above, cationic shell layers containing a thermosetting resin (melamine resin) were formed over the surface of the cores. As a result of the above process, a dispersion of toner mother particles was obtained. Next, the dispersion was adjusted to pH 7 (i.e., neutralized) through addition of sodium hydroxide. The dispersion was subsequently cooled to room temperature (25° C.).

(Washing and Drying)

Once the toner mother particles (cores and shell layers) had been formed, the dispersion of the toner mother particles was subjected to vacuum filtration (i.e., solid-liquid separation) using a Buchner funnel (Nutsche filter). A wet cake of the toner mother particles was obtained through the vacuum filtration. Next, the toner mother particles were dispersed in ion exchanged water. The toner mother particles were washed by repeating steps of filtration and dispersion. The steps of filtration and dispersion were repeated until 10 g of the toner mother particles dispersed in 100 g of ion exchanged water had an electrical conductivity of no greater than 4 µS/cm. It is thought that so long as the electrical conductivity of the aforementioned dispersion is no greater than 10 µS/cm, there is no significant effect on chargeability of the toner. The electrical conductivity was measured using a HORIBA ES-51 electrical conductivity meter produced by HORIBA, Ltd. The filtrates contained almost none of the shell material (monomer or resin) that had been added. The filtrates after washing had a TOC concentration of no greater than 8 mg/L. The TOC concentration was measured using an online TOC analyzer (TOC-4200 produced by Shimadzu Corporation).

Next, the washed wet cake of toner mother particles was broken up and the toner mother particles were dried using a vacuum oven.

The shell layer thickness of the toner mother particles was measured according to the following method.

First, a plurality of toner mother particles were dispersed in a cold-setting epoxy resin and left to stand for two days at an ambient temperature of 40° C. to obtain a hardened material. The hardened material was dyed in osmium tetroxide and subsequently a flake sample was cut therefrom using an ultramicrotome (EM UC6 manufactured by Leica Microsystems) equipped with a diamond knife. Next, a transmission electron microscopy (TEM) image of a cross-section of the flake sample was captured using a transmission electron microscope (JSM-6700F produced by JEOL Ltd.).

The shell layer thickness was measured by analyzing the TEM image using image analysis software (WinROOF produced by Mitani Corporation). More specifically, on a cross-section of a toner particle, two straight lines were drawn to intersect at right angles at approximately the center of the cross-section. The lengths of four line segments overlapping with the shell layer were measured, thereby measuring thickness of the shell layer at four locations. The shell layer thickness of the toner particle subjected to measurement was determined to be the arithmetic mean of the four lengths that were measured. The shell layer thickness was measured with respect to each of an appropriate number of toner particles (for example, 10 particles) included in the toner. The arithmetic mean of at least 10 measured values was used as an evaluation value.

When the shell layer is excessively thin, the TEM image may not clearly depict a boundary between the core and the shell layer, complicating measurement of thickness of the shell layer. In such a situation, the thickness of the shell layer was measured by using TEM and electron energy loss spectroscopy (EELS) in combination in order to clarify the boundary between the core and the shell layer. More specifically, in the captured TEM image, mapping was performed by EELS for an element (for example, nitrogen) contained in the shell layer.

Toner A had a shell layer thickness of 10 nm as measured according to the method described above. Also, the shell layers of toner A contained a thermoplastic unit and a thermosetting unit. More specifically, in the shell layers of toner A, the thermoplastic unit was cross-linked by the thermosetting unit. In toner A, the thermoplastic unit contained an acrylic component based on an acrylamide resin. Also, in toner A, the thermosetting unit was derived from methylol melamine.

(External Addition)

First, 100 parts by mass of the dried toner mother particles and 1 part by mass of dry silica fine particles (REA90 produced by Nippon Aerosil Co., Ltd.) were mixed using a mixer having a capacity of 5 L (FM mixer produced by Nippon Coke & Engineering Co., Ltd.). The mixing caused the external additive (i.e., the dry silica fine particles) to adhere to the surface of the toner mother particles. Through the above process, toner A including a large number of toner particles was obtained.

The following explains preparation methods of toners B-G. Note that unless specifically stated, the evaluation method of toners B-G was the same as the evaluation method of toner A. Each of toners B-E and G had a shell layer thickness of 10 nm. Toner F had a shell layer thickness of 50 nm.

[Preparation Method of Toner B]

In the preparation method of toner B, the volume ratio of material additive amounts (i.e., a ratio MIRBANE resin SM-607:BECKAMINE A-1) during shell layer formation

was 8:2 (=4:1) instead of 5:5 (=1:1), but in all other aspects toner B was prepared according to the same method as toner A.

[Preparation Method of Toner C]

In the preparation method of toner C, the volume ratio of material additive amounts (i.e., a ratio MIRBANE resin SM-607:BECKAMINE A-1) during shell layer formation was 2:8 (=1:4) instead of 5:5 (=1:1), but in all other aspects toner C was prepared according to the same method as toner A.

[Preparation Method of Toner D]

In the preparation method of toner D, 1 mL of an acrylic emulsion (VONCOAT AN-1170 produced by DIC Corporation; solid component concentration 50% by mass) was used during shell layer formation instead of 2 mL of the aqueous solution of acrylamide resin (BECKAMINE A-1), but in all other aspects toner D was prepared according to the same method as toner A. In the preparation method of toner D, the additive amount of the aqueous solution of hexamethylol melamine prepolymer (MIRBANE resin SM-607 produced by Showa Denko K.K.; solid component concentration 80% by mass) was 1 mL.

[Preparation Method of Toner E]

In the preparation method of toner E, the volume ratio of material additive amounts (i.e., a ratio MIRBANE resin SM-607:BECKAMINE A-1) during shell layer formation was 10:0 instead of 5:5 (=1:1), but in all other aspects toner E was prepared according to the same method as toner A. In the preparation method of toner E, the additive amount of the aqueous solution of hexamethylol melamine prepolymer (MIRBANE resin SM-607 produced by Showa Denko K.K.; solid component concentration 80% by mass) was 4 mL. In the preparation method of toner E, the aqueous solution of acrylamide resin (BECKAMINE A-1) was not added.

[Preparation Method of Toner F]

In the preparation method of toner F, the volume ratio of material additive amounts (i.e., a ratio MIRBANE resin SM-607:VONCOAT AN-1170) during shell layer formation was 0:10 instead of 5:5 (=1:1), but in all other aspects toner F was prepared according to the same method as toner D. In the preparation method of toner F, the additive amount of the acrylic emulsion (VONCOAT AN-1170 produced by DIC Corporation; solid component concentration 50% by mass) was 10 mL. In the preparation method of toner F, the aqueous solution of hexamethylol melamine prepolymer (MIRBANE resin SM-607) was not added.

[Preparation Method of Toner G]

In the preparation method of toner G, 1 mL of a thermoplastic styrene-acrylic emulsion (POLYSOL MC-5 produced by Showa Denko K.K.; solid component concentration 50% by mass) was used during shell layer formation instead of 2 mL of the aqueous solution of acrylamide resin (BECKAMINE A-1), but in all other aspects toner G was prepared according to the same method as toner A. In the preparation method of toner G, the additive amount of the aqueous solution of hexamethylol melamine prepolymer (MIRBANE resin SM-607 produced by Showa Denko K.K.; solid component concentration 80% by mass) was 1 mL.

[Evaluation Method]

The following explains an evaluation method used for each of the samples (toners A-G).

(Hardness)

Evaluation was performed using, as an evaluation device, a scanning probe station (NanoNaviReal produced by Hitachi High-Tech Science Corporation) equipped with an SPM (S-image produced by Hitachi High-Tech Science Corporation) having an internal heater. Prior to measurement, the

evaluation device was calibrated using poly(methyl methacrylate) (PMMA) particles of particle diameter 10  $\mu\text{m}$  as a calibration reference material with an allowable range of  $2.920 \pm 0.119$  GPa (Young's modulus at 30° C.). The Young's modulus of the PMMA at 30° C. as measured after calibration of the evaluation device was 3.01 GPa.

The toner mother particles of a sample (any one of toners A-G) were cleaved and mounted on a measurement table of the evaluation device. The evaluation device was used to plot a force curve for a cross-section of the toner mother particles. Note that the toner mother particles subjected to measurement corresponded to toner particles of the sample (any one of toners A-G) prior to external addition. Prior to measurement, the toner mother particles were left for 10 hours at an ambient temperature of 22° C. and an ambient humidity of at least 50% RH and no greater than 60% RH. The toner mother particles subjected to measurement had a particle diameter of 6  $\mu\text{m}$ .

The force curve was converted to a "load/pressing distance" curve and a localized Young's modulus was calculated. Measurement of the Young's modulus was performed while changing the temperature of a cantilever of the SPM in a range from 30° C. to 70° C. More specifically, the cantilever temperature of the SPM was increased at a heating rate of 5° C./s and measurements of hardness (Young's modulus) of the cross-sections of the toner mother particles were performed at cantilever temperatures of 30° C., 50° C., and 70° C. More specifically, for each of 10 toner mother particles included in the toner, the hardness (Young's modulus) was measured at six locations (three locations corresponding to the core and three locations corresponding to the shell layer), thereby obtaining 30 measured values for the cores and 30 measured values for the shell layers. The arithmetic mean of the 30 measured values was used as an evaluation value.

A proportion of change of the Young's modulus of the cores from 30° C. to 50° C. (herein referred to as a first proportion of hardness change) and a proportion of change of the Young's modulus of the cores from 50° C. to 70° C. (herein referred to as a second proportion of hardness change) were measured based on the following expressions. A first proportion of hardness change and a second proportion of hardness change were measured in the same manner for the shell layers.

$$\text{First proportion of hardness change (\%)} = 100 \times \frac{|\text{Young's modulus at } 30^\circ \text{ C.} - \text{Young's modulus at } 50^\circ \text{ C.}|}{\text{Young's modulus at } 30^\circ \text{ C.}}$$

$$\text{Second proportion of hardness change (\%)} = 100 \times \frac{|\text{Young's modulus at } 50^\circ \text{ C.} - \text{Young's modulus at } 70^\circ \text{ C.}|}{\text{Young's modulus at } 50^\circ \text{ C.}}$$

Note that the first proportion of hardness change and the second proportion of hardness change are both absolute values.

Herein, a value obtained by dividing the first proportion of hardness change for the cores by the first proportion of hardness change for the shell layers as shown below is referred to as a ratio of first proportions of hardness change. A value obtained by dividing the second proportion of hardness change for the cores by the second proportion of hardness change for the shell layers as shown below is referred to as a ratio of second proportions of hardness change.

$$\text{Ratio of first proportions of hardness change} = \frac{\text{first proportion of hardness change for cores}}{\text{first proportion of hardness change for shell layers}}$$

$$\text{Ratio of second proportions of hardness change} = \frac{\text{second proportion of hardness change for cores}}{\text{second proportion of hardness change for shell layers}}$$

In evaluation of each of the samples (toners A-G), hardness of the toner mother particles was measured prior to external addition. However, the toners may be evaluated according to a different method. For example, the external additive may be removed from the toner particles after external addition thereof, and hardness of the toner mother particles obtained thereby may be measured. The external additive can for example be removed from the toner particles by using an alkaline solution (for example, an aqueous solution of sodium hydroxide) to dissolve the external additive. Alternatively, the external additive may for example be removed from the toner particles using an ultrasonic washer. In a situation in which it is difficult to measure the Young's modulus of a shell layer by applying the cantilever to the shell layer as exposed in the cross-section of the toner mother particle (for example, when the shell layer is extremely thin), the Young's modulus of the shell layer may be measured by applying the cantilever to the shell layer as exposed at the surface of the toner mother particle.

#### (Fixability)

Fixability was evaluated using a printer (FS-C5250DN produced by KYOCERA Document Solutions Inc., modified to enable adjustment of fixing temperature) having a roller-roller type heat-pressure fixing section (nip width 8 mm) as an evaluation device. A two-component developer was prepared by mixing 100 parts by mass of a developer carrier (carrier for FS-C5250DN) and 10 parts by mass of a sample (toner) for 30 minutes using a ball mill. The two-component developer that was prepared was loaded into a developing section of the evaluation device and the sample (toner) was loaded into a toner container of the evaluation device.

The evaluation device was used to convey 90 g/m<sup>2</sup> paper at a linear velocity of 200 mm/s and to develop 1.0 mg/cm<sup>2</sup> of toner on the paper during conveyance. The toner was used to form a solid image. After development, the paper was passed through the fixing section. The transit time of the paper through a nip of the fixing section was 40 ms. The fixing temperature was set in a range from 100° C. to 200° C. More specifically, a minimum temperature at which the toner (solid image) was fixable to the paper (i.e., a minimum fixing temperature) was measured by increasing the fixing temperature of the fixing section from 100° C. in increments of 5° C. Determination of whether or not the toner was fixable at a given temperature was carried out through a fold-rubbing test such as described below (i.e., by measuring the length of toner peeling at a fold).

The fold-rubbing test was performed by folding the paper in half such that a surface on which the image was formed was folded inwards, and by rubbing a 1 kg weight covered with cloth back and forth on the fold five times. Next, the paper was opened up and a fold portion (i.e., a portion to which the solid image was fixed) was observed. The length of toner peeling of the fold portion (peeling length) was measured. The minimum fixing temperature was determined to be the lowest temperature among temperatures for which the peeling length was no greater than 1 mm.

A minimum fixing temperature of no greater than 160° C. was evaluated as good and a minimum fixing temperature of greater than 160° C. was evaluated as poor.

#### (Preservability)

First, 2 g of a sample (toner) was placed in a plastic container having a capacity of 20 mL and the plastic container was left to stand for three hours in a thermostatic chamber set to 60° C. Through the above, an evaluation toner was obtained. The evaluation toner was cooled to 20° C. for three hours and was then placed on a 100-mesh sieve of known mass. The mass of the toner prior to sifting was calculated by

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measuring the total mass of the sieve and the toner thereon. Next, the sieve was placed in a powder tester (product of Hosokawa Micron Corporation) and the evaluation toner was sifted in accordance with a manual of the powder tester by shaking the sieve for 30 seconds at a rheostat level of 5. After the sifting, the mass of toner remaining on the sieve was calculated by once again measuring the total mass of the sieve and the toner thereon. Aggregation of the toner (% by mass) was calculated from the mass of the toner prior to sifting and the mass of the toner after sifting (mass of the toner remaining on the sieve after sifting) based on the expression shown below.

$$\text{Aggregation (\% by mass)} = 100 \times \frac{\text{mass of toner after sifting}}{\text{mass of toner prior to sifting}}$$

Aggregation of no greater than 20% by mass was evaluated as good and aggregation of greater than 20% by mass was evaluated as poor.

## [Evaluation Results]

Table 2 summarizes the results for measurement of hardness. In Table 2, "S" denotes the shell layers and "C" denotes the cores.

TABLE 2

| Measurement | target | Young's modulus |        |        | Proportion of change of Young's modulus (%) |                  | C/S |      |
|-------------|--------|-----------------|--------|--------|---|------------------|-----|------|
|             |        | (GPa)           |        |        | 30° C. to 50° C.                            | 50° C. to 70° C. |     |      |
|             |        | 30° C.          | 50° C. | 70° C. | (X)   | (Y)              | X   | Y    |
| Toner A     | S      | 3.52            | 3.34   | 3.00   | 5.1   | 10.2             | 3.0 | 5.9  |
|             | C      | 2.75            | 2.33   | 0.93   | 15.3  | 60.1             |     |      |
| Toner B     | S      | 3.98            | 3.78   | 3.40   | 5.0   | 10.1             | 3.1 | 6.0  |
|             | C      | 2.75            | 2.33   | 0.93   | 15.3  | 60.1             |     |      |
| Toner C     | S      | 3.20            | 2.97   | 2.52   | 7.2   | 15.2             | 3.5 | 4.8  |
|             | C      | 2.70            | 2.02   | 0.54   | 25.2  | 73.3             |     |      |
| Toner D     | S      | 3.20            | 2.97   | 2.52   | 7.2   | 15.2             | 4.2 | 5.3  |
|             | C      | 2.70            | 1.89   | 0.37   | 30.0  | 80.4             |     |      |
| Toner E     | S      | 3.57            | 3.46   | 3.35   | 3.1   | 3.2              | 5.1 | 18.1 |
|             | C      | 2.85            | 2.40   | 1.02   | 15.8  | 57.5             |     |      |
| Toner F     | S      | 2.78            | 1.94   | 0.97   | 30.2  | 50.0             | 0.5 | 1.2  |
|             | C      | 2.70            | 2.27   | 0.88   | 15.9  | 61.2             |     |      |
| Toner G     | S      | 3.00            | 2.40   | 1.44   | 20.0  | 40.0             | 1.4 | 1.3  |
|             | C      | 2.70            | 1.94   | 0.97   | 28.1  | 50.0             |     |      |

For toner A, the Young's modulus of the shell layers was 3.52 GPa at 30° C., 3.34 GPa at 50° C., and 3.00 GPa at 70° C. The Young's modulus of the cores was 2.75 GPa at 30° C., 2.33 GPa at 50° C., and 0.93 GPa at 70° C. The first proportion of hardness change (X1) for the shell layers was 5.1%, the first proportion of hardness change (X2) for the cores was 15.3%, the second proportion of hardness change (Y1) for the shell layers was 10.2%, and the second proportion of hardness change (Y2) for the cores was 60.1%. The ratio of first proportions of hardness change (X2/X1) was 3.0 and the ratio of second proportions of hardness change (Y2/Y1) was 5.9.

For toner B, the Young's modulus of the shell layers was 3.98 GPa at 30° C., 3.78 GPa at 50° C., and 3.40 GPa at 70° C. The Young's modulus of the cores was 2.75 GPa at 30° C., 2.33 GPa at 50° C., and 0.93 GPa at 70° C. The first proportion of hardness change (X1) for the shell layers was 5.0%, the first proportion of hardness change (X2) for the cores was 15.3%, the second proportion of hardness change (Y1) for the shell layers was 10.1%, and the second proportion of hardness change (Y2) for the cores was 60.1%. The ratio of first proportions of hardness change (X2/X1) was 3.1 and the ratio of second proportions of hardness change (Y2/Y1) was 6.0.

For toner C, the Young's modulus of the shell layers was 3.20 GPa at 30° C., 2.97 GPa at 50° C., and 2.52 GPa at 70°

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C. The Young's modulus of the cores was 2.70 GPa at 30° C., 2.02 GPa at 50° C., and 0.54 GPa at 70° C. The first proportion of hardness change (X1) for the shell layers was 7.2%, the first proportion of hardness change (X2) for the cores was 25.2%, the second proportion of hardness change (Y1) for the shell layers was 15.2%, and the second proportion of hardness change (Y2) for the cores was 73.3%. The ratio of first proportions of hardness change (X2/X1) was 3.5 and the ratio of second proportions of hardness change (Y2/Y1) was 4.8.

For toner D, the Young's modulus of the shell layers was 3.20 GPa at 30° C., 2.97 GPa at 50° C., and 2.52 GPa at 70° C. The Young's modulus of the cores was 2.70 GPa at 30° C., 1.89 GPa at 50° C., and 0.37 GPa at 70° C. The first proportion of hardness change (X1) for the shell layers was 7.2%, the first proportion of hardness change (X2) for the cores was 30.0%, the second proportion of hardness change (Y1) for the shell layers was 15.2%, and the second proportion of hardness change (Y2) for the cores was 80.4%. The ratio of first proportions of hardness change (X2/X1) was 4.2 and the ratio of second proportions of hardness change (Y2/Y1) was 5.3.

For toner E, the Young's modulus of the shell layers was 3.57 GPa at 30° C., 3.46 GPa at 50° C., and 3.35 GPa at 70°

C. The Young's modulus of the cores was 2.85 GPa at 30° C., 2.40 GPa at 50° C., and 1.02 GPa at 70° C. The first proportion of hardness change (X1) for the shell layers was 3.1%, the first proportion of hardness change (X2) for the cores was 15.8%, the second proportion of hardness change (Y1) for the shell layers was 3.2%, and the second proportion of hardness change (Y2) for the cores was 57.5%. The ratio of first proportions of hardness change (X2/X1) was 5.1 and the ratio of second proportions of hardness change (Y2/Y1) was 18.1.

For toner F, the Young's modulus of the shell layers was 2.78 GPa at 30° C., 1.94 GPa at 50° C., and 0.97 GPa at 70° C. The Young's modulus of the cores was 2.70 GPa at 30° C., 2.27 GPa at 50° C., and 0.88 GPa at 70° C. The first proportion of hardness change (X1) for the shell layers was 30.2%, the first proportion of hardness change (X2) for the cores was 15.9%, the second proportion of hardness change (Y1) for the shell layers was 50.0%, and the second proportion of hardness change (Y2) for the cores was 61.2%. The ratio of first proportions of hardness change (X2/X1) was 0.5 and the ratio of second proportions of hardness change (Y2/Y1) was 1.2.

For toner G, the Young's modulus of the shell layers was 3.00 GPa at 30° C., 2.40 GPa at 50° C., and 1.44 GPa at 70° C. The Young's modulus of the cores was 2.70 GPa at 30° C.,

1.94 GPa at 50° C., and 0.97 GPa at 70° C. The first proportion of hardness change (X1) for the shell layers was 20.0%, the first proportion of hardness change (X2) for the cores was 28.1%, the second proportion of hardness change (Y1) for the shell layers was 40.0%, and the second proportion of hardness change (Y2) for the cores was 50.0%. The ratio of first proportions of hardness change (X2/X1) was 1.4 and the ratio of second proportions of hardness change (Y2/Y1) was 1.3.

Table 3 summarizes the results of evaluation of fixability and preservability for each of toners A-G.

TABLE 3

| Toner   | Fixability<br>(° C.) | Preservability<br>(% by mass) |
|---------|----------------------|-------------------------------|
| Toner A | 150                  | 8                             |
| Toner B | 140                  | 5                             |
| Toner C | 155                  | 18                            |
| Toner D | 145                  | 15                            |
| Toner E | 170                  | 3                             |
| Toner F | 150                  | 50                            |
| Toner G | 150                  | 90                            |

For each of toners A-D, F, and G, the minimum fixing temperature was no greater than 160° C. For toner E, the minimum fixing temperature was greater than 160° C.

For each of toners A-E, aggregation was no greater than 20% by mass. For each of toners F and G, aggregation was greater than 20% by mass.

As explained above, for each of toners A-D (herein referred to as toners according to the present Examples), X2 was greater than X1. Also, X2/X1 was at least 2.0 and no greater than 5.0 (more specifically, at least 3.0 and no greater than 4.2), and Y2/Y1 was at least 4.0 and no greater than 7.0 (more specifically, at least 4.8 and no greater than 6.0). Note that X1 denotes the first proportion of hardness change for the shell layers (i.e., the proportion of change of the Young's modulus of the shell layers upon raising the cantilever temperature from 30° C. to 50° C.). X2 denotes the first proportion of hardness change for the cores (i.e., the proportion of change of the Young's modulus of the cores upon raising the cantilever temperature from 30° C. to 50° C.). Y1 denotes the second proportion of hardness change for the shell layers (i.e., the proportion of change of the Young's modulus of the shell layers upon raising the cantilever temperature from 50° C. to 70° C.). Y2 denotes the second proportion of hardness change for the cores (i.e., the proportion of change of the Young's modulus of the cores upon raising the cantilever temperature from 50° C. to 70° C.). Each of the toners according to the present Examples had good high-temperature preservability and low-temperature fixability.

Furthermore, for each of toners A and B, X2 was no greater than 20.0%. As shown in Table 3, each of toners A and B had a minimum fixing temperature of no greater than 150° C. and aggregation of no greater than 10% by mass. Therefore, each of toners A and B had especially good high-temperature preservability and low-temperature fixability.

For each of the toners relating to the present Examples, the Young's modulus of the shell layers as measured when the cantilever temperature of the SPM was 30° C. was at least 3.00 GPa and no greater than 4.00 GPa (more specifically, at least 3.20 GPa and no greater than 3.98 GPa). Also, the Young's modulus of the cores as measured when the cantilever temperature of the SPM was 30° C. was at least 2.50 GPa and no greater than 2.80 GPa (more specifically, at least 2.70 GPa and no greater than 2.75 GPa). For each of the toners according to the present Examples, the thickness of the shell

layers was at least 1 nm and no greater than 20 nm (more specifically, 10 nm). In each of the toners according to the present Examples, the thermoplastic unit contained an acrylic component (i.e., an acrylic component based on an acrylamide resin or an acrylic emulsion). Also, in each of the toners according to the present Examples, the thermosetting unit was a unit derived from a monomer or prepolymer of a melamine resin (more specifically, methylol melamine).

The present disclosure is of course not limited to the Examples described above.

A toner is considered to have good high-temperature preservability and low-temperature fixability when satisfying conditions that: the first proportion of hardness change for the cores is greater than the first proportion of hardness change for the shell layers; division of the first proportion of hardness change for the cores by the first proportion of hardness change for the shell layers yields a value of at least 2.0 and no greater than 5.0; and division of the second proportion of hardness change for the cores by the second proportion of hardness change for the shell layers yields a value of at least 4.0 and no greater than 7.0.

What is claimed is:

1. A toner comprising

a plurality of toner particles each including:

a core; and

a shell layer disposed over a surface of the core, wherein the shell layer contains a unit derived from a thermoplastic resin and a unit derived from a monomer or prepolymer of a thermosetting resin, and

a Young's modulus of the core and a Young's modulus of the shell layer, as measured using a scanning probe microscope while raising a cantilever temperature thereof, satisfy conditions:

X2/X1 is at least 2.0 and no greater than 5.0; and

Y2/Y1 is at least 4.0 and no greater than 7.0,

where X1 denotes a proportion of change of the Young's modulus of the shell layer upon raising the cantilever temperature from 30° C. to 50° C., X2 denotes a proportion of change of the Young's modulus of the core upon raising the cantilever temperature from 30° C. to 50° C., Y1 denotes a proportion of change of the Young's modulus of the shell layer upon raising the cantilever temperature from 50° C. to 70° C., and Y2 denotes a proportion of change of the Young's modulus of the core upon raising the cantilever temperature from 50° C. to 70° C.,

the core contains a polyester resin,

the unit derived from the thermoplastic resin contains an acrylic component, and

the unit derived from the monomer or prepolymer of the thermosetting resin is a unit derived from a monomer or prepolymer of a melamine resin.

2. A toner according to claim 1, wherein

X2 is no greater than 20.0%.

3. A toner according to claim 1, wherein

the Young's modulus of the shell layer as measured using the scanning probe microscope when the cantilever temperature is 30° C. is at least 3.00 GPa and no greater than 4.00 GPa.

4. A toner according to claim 1, wherein

the Young's modulus of the core as measured using the scanning probe microscope when the cantilever temperature is 30° C. is at least 2.50 GPa and no greater than 2.80 GPa.



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5. A toner according to claim 1, wherein the shell layer has a thickness of at least 1 nm and no greater than 20 nm.

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